



Decomplexation of Cu(II)-EDTA by UV/persulfate and UV/H₂O₂: Efficiency and mechanism

Zhe Xu, Chao Shan, Bihuang Xie, Yan Liu, Bingcai Pan*

State Key Laboratory of Pollution Control and Resource Reuse, School of the Environment, Nanjing University, Nanjing 210023, China



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ABSTRACT

Heavy metal-organic complexes are widely present in natural water and industrial effluents. Currently, the widely employed strategy for removal of metal-organic complexes is to combine oxidative decomposition with further precipitation or adsorption of the released metals. •OH and SO₄^{•-} based advanced oxidation processes (AOPs) are very promising in water purification. However, to the best of our knowledge, there is no open literature concerning the decomplexation efficiency of metal-organic complexes based on SO₄^{•-} as yet. In this study, a typical SO₄^{•-} based technology, i.e., UV/PS (persulfate) process, was applied to investigate its decomplexation of Cu(II)-EDTA in water, and the final Cu(II) removal during the subsequent alkaline precipitation was used as a reference of the decomplexation efficiency. UV/H₂O₂ was employed for comparison throughout the study. Effect of the oxidant dosage, pH, and coexisting substances on the decomplexation was evaluated, and the degradation mechanism was particularly concerned. The results show that degradation of Cu(II)-EDTA by SO₄^{•-} and •OH follows a similar pathway, i.e., successive decarboxylation, while the decomplexation efficiency of UV/PS is much higher than UV/H₂O₂ under similar conditions. Meanwhile, the coexisting substances (Cl⁻, NO₃⁻, and NOM) exerted less inhibition on the decomplexation of UV/PS than UV/H₂O₂. The above advantages of UV/PS are mainly attributed to the better selectivity of SO₄^{•-} as well as its higher yield of active species. Similarly, satisfactory performance was observed for Cu-citrate and Cu-nitrilotriacetate removal from aqueous solution and for Cu(II) removal from a real electroplating effluent as well, further demonstrating the promising applicability of the UV/PS based combined process in water decontamination from Cu-organic complexes.

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1. Introduction

Heavy metals are ubiquitous in natural water and industrial wastewater, and their adverse effect on human and environment has been extensively investigated and well documented [1–3]. Nowadays, increasingly stringent regulations have been made to mitigate heavy metal pollution in both drinking water and industrial effluents. Generally speaking, free metal ions in water can be readily removed through the traditional processes such as precipitation, adsorption and ion exchange. Except for free ions, heavy metals tend to form stable organic complexes by receiving electron pair from some functional groups, e.g. carboxyl, amino, phenolic hydroxyl and mercapto groups [4]. Such complexation not only enhances the mobility of heavy metals in natural water, but makes them refractory to the traditional methods mentioned above. As reported previously [5,6], adsorption and chemical pre-

cipitation cannot achieve satisfactory treatment for metal-organic complexes, and new processes are still urgently required to eliminate the metal complexes from water.

In the past years, a variety of new processes have been developed to dispose of the heavy metal complexes, e.g. membrane filtration, electrolysis, oxidation and combined processes [6–8], among which the advanced oxidation processes (AOPs) based on hydroxyl radical (•OH) have received increasing interest due to the strong oxidation power of •OH ($E^{\circ} = 2.4\text{--}3.0\text{ V}$). The typical AOPs, including Fenton, photo-Fenton, UV-TiO₂, UV/H₂O₂ and ozonation, have been verified to be capable of destroying the ligands [9–11], where the heavy metals will be released as free ions and further eliminated by other traditional methods.

As an alternative to •OH based AOPs, sulfate radicals (SO₄^{•-}) based oxidation technology has attracted increasing attention over the past decade. SO₄^{•-} exhibits similar redox potential to •OH ($E^{\circ} = 2.6\text{--}3.2\text{ V}$) [12] and could be generated through activation of persulfate (PS) and peroxymonosulfate (PMS) or other radical pathways [13–17]. To date, SO₄^{•-} based oxidation has been successfully applied in removing abundant toxic substances from

* Corresponding author.

E-mail address: bcpn@nju.edu.cn (B. Pan).

water [18–20]. Compared to $\cdot\text{OH}$, which reacts rapidly with organic substrates through hydrogen abstraction, electron transfer and/or addition reaction, $\text{SO}_4^{\bullet-}$ exhibits slower kinetics of hydrogen abstraction and prefers to attack nucleophile structures via electron transfer. In other words, it possesses better selectivity toward organic degradation [21,22]. Meanwhile, the negatively charged $\text{SO}_4^{\bullet-}$ may be more sensitive to solution chemistry and electrical property of the target substance [23,24]. Thus, different mechanisms were reported for oxidation of an identical compound by $\cdot\text{OH}$ and $\text{SO}_4^{\bullet-}$ [25,26]. Similarly, it is reasonable to anticipate that $\cdot\text{OH}$ and $\text{SO}_4^{\bullet-}$ may show different decomplexation efficiency and oxidation mechanism toward heavy metal complexes.



To the best of our knowledge, though several studies are available concerning the activation of PS by metal complexes [21,27], till now little is known about the degradation of heavy metal complexes by $\text{SO}_4^{\bullet-}$ based oxidation technology. Herein, the UV/PS process, a typical $\text{SO}_4^{\bullet-}$ based oxidation technology, was employed to evaluate its efficiency on the decomplexation of Cu(II)-EDTA under varying conditions, and the underlying mechanism was particularly concerned. A systematic comparison between UV/PS and UV/ H_2O_2 was performed throughout the study to illuminate their different properties on the degradation of Cu(II)-EDTA. The subsequent alkaline precipitation was employed to remove the free or weakly complexed Cu(II) generated during the oxidation, and the final Cu removal was employed as an index to evaluate the efficiency of both oxidation processes.

2. Materials and experiments

2.1. Reagents

All reagents are of analytic grade or higher purity, and used without further purification. Ethylene-diaminetetraacetic acid copper (II) disodium salt (Cu(II)-EDTA), potassium persulfate ($\text{K}_2\text{S}_2\text{O}_8$), ethylenediaminetetraacetic acid (EDTA), ethylenediamine-N,N'-diacetic acid (N,N'-ED2A), sodium iminodiacetate dibasic hydrate (IMDA), nitrilotriacetic acid trisodium salt (NTA), sodium formate, ethylenediamine (EDA) and glycine were purchased from Sigma-Aldrich. In addition, N-(2-aminoethyl)glycine (EDMA) from Tokyo Chemical Industry (TCI), 30% hydrogen peroxide (H_2O_2) from Alfa Aesar, dimethyl pyridine N-oxide (DMPO) from J&K Chemical, Suwannee river natural organic matter (SRNOM) from the International Humic Substance Society (St. Paul, MN, USA) and methanol and acetonitrile from Merck KGaA were employed for this study. Other reagents were provided by Sinopharm Chemical Reagent Co., Ltd. All the stock solutions were stored in the dark environment. The PS solution was prepared daily to avoid its thermal decomposition and hydrolysis. The UV light was generated by a 254 nm low pressure mercury lamp (Heraeus, 10 W) which was covered by a copper gauze. A cylindrical quartz reactor (8.0 cm in diameter) was put 12.5 cm away from the UV lamp (the light intensity at the center of the quartz reactor was measured to be 0.25 mW/cm²).

2.2. Experimental procedure

2.2.1. Degradation experiment

A desired volume of Cu(II)-EDTA solution at the preset level was first added into the quartz reactor, and then appropriate dosage of PS or H_2O_2 was injected, ensuring the final volume of the reaction solution of 200 mL. After the addition of the oxidant, the reactor was subjected to UV irradiation immediately. The mercury lamp

was warmed up for at least 15 min prior to use, pH was *in situ* monitored, and NaOH or H_2SO_4 solution was added when necessary to maintain a constant pH value during the oxidation. The solution sampled at different intervals was immediately added with the quencher, i.e., 2.0 M methanol or 0.2 M sodium nitrite (for TOC analysis only), to terminate the reaction. Each sample was refrigerated before analysis or further treatment.

To determine the direct reaction activity between Cu(II) complex and PS/ H_2O_2 , 2.5 M methanol and 1.0 M tert butyl alcohol (TBA) were pre-added to the solution to block the degradation by radicals (and possible Cu(III)) before the addition of H_2O_2 or PS. Then, the reaction was initiated by adding 18 mM PS or H_2O_2 , and lasted 90 min.

2.2.2. Chemical precipitation

The NaOH solution (1.0 M) was added dropwise to the oxidized samples until the pH increased to 11.0, and then each sample was placed for 5 h to ensure a complete precipitation. Then, the supernate was filtered by a 0.22-μm filter to measure the residual copper in the filtrate. The precipitate was freeze-dried for X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) analysis. Note that all the above experiments were performed duplicate at $20 \pm 1^\circ\text{C}$ for data analysis.

2.3. Analysis

The concentration of H_2O_2 was detected through the I_3^- method [28], and that of PS was determined according to the method developed by Liang et al. [29]. The light intensity was measured by a radiometer (Photoelectric Instrument Factory of Beijing Normal University, China) equipped with a sensor with peak sensitivity at 254 nm. Flame/graphite furnace atomic absorption spectrophotometer was applied to measure total copper concentration in solution (Shimadzu AA-7000). TOC in solution was identified by total organic carbon analyzer (Shimadzu-L). UV-vis spectrophotometer was used to detect the absorption spectrum of the test solution.

To identify the degradation products of Cu(II)-EDTA, 30 mM Cu(II)-EDTA was applied for oxidation, where the molar ratio of PS and H_2O_2 to Cu(II)-EDTA was set as 50:1 and 150:1 respectively, and the irradiation intensity was set as 0.8 mW/cm². The concentration of the degradation products was detected by capillary electrophoresis (P/ACETM MDQ series capillary electrophoresis system), where a silica capillary of 75 μm in inner diameter and 50 cm in length was applied, and 50 mM borate with 1 mM cetyl trimethyl ammonium bromide was used as the carrier electrolyte. Reverse voltage of 10 or 16 kV was used to separate each species, and the detection wavelength was set as 254 nm. The effluence sequence of Cu complexes is: Cu-IMDA, Cu(II)-EDTA, Cu-NTA, Ethylene-diametriacetic acid copper (Cu-ED3A), Cu-ED2A and other substances (Cu-EDMA, Cu-glycine, Cu-EDA) respectively. To evaluate the direct photolysis of every possible Cu-complex and their reactivity toward PS and H_2O_2 , every ligand before and after the photolysis/reaction was quantified by HPLC (Dionex ultimate-3000) equipped with Waters XBridge column (150 mm, 3.5 μm particle size). The mobile phase was acetonitrile/formic (3:97, v/v), and the detection wavelength was 203 nm. Prior to HPLC measurement, adequate EDTA was added to the test solution, which was shaken for 1 h to fully release the target ligand from Cu complexes for further analysis. This is because the coordination constant of EDTA toward Cu(II) is several order of magnitude higher than other organic ligands (i.e., the degradation intermediates/products)

Electronic paramagnetic resonance (EPR) spectrometer (Bruker EMX-10/12) with a 300 W high pressure mercury lamp was applied to obtain the information of the active species during oxidation. To carry out the EPR measurement, each stock solution and sample

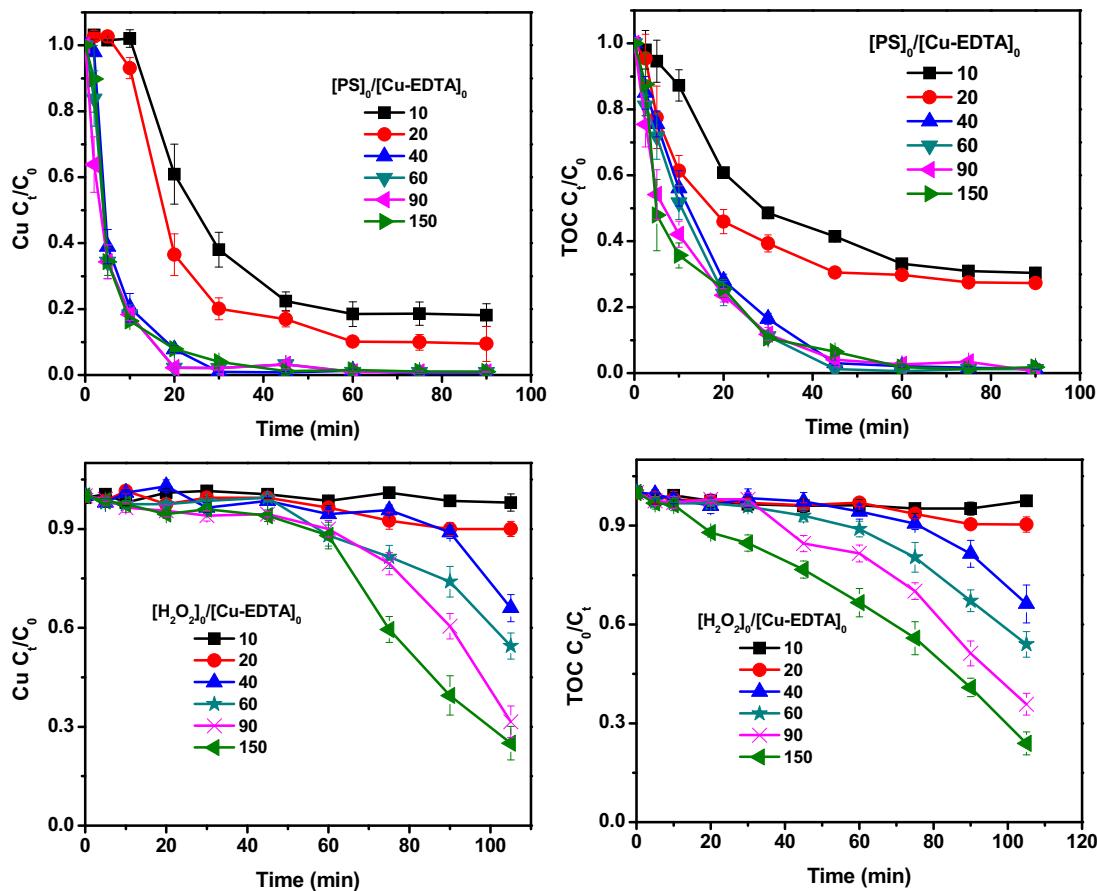


Fig. 1. Effect of the oxidant dosage (in molar ratio) on Cu and TOC removal in UV/PS and UV/H₂O₂ processes ($[\text{Cu(II)}\text{-EDTA}]_0 = 0.30 \text{ mM}$, pH during the irradiation = 4.0 ± 0.2 , pH for precipitation = 11.0, irradiation intensity = 0.25 mW/cm^2 , temperature = $20 \pm 1^\circ\text{C}$).

were prepared freshly, and the test sample with a preset composition was mixed with DMPO to attain its final concentration of 83.3 mM. Then, the mixture was immediately injected into a quartz capillary for analysis under irradiation or dark conditions. XPS spectra of the resultant precipitates was recorded to probe the electron binding energy of Cu(II) (UIVAC-PHI PHI 5000 VersaProbe), and their crystal form was identified by XRD (ARL X'TRA).

3. Results and discussion

3.1. Effect of oxidants concentration

Efficiency of Cu(II) removal by UV/PS and UV/H₂O₂ followed by alkaline precipitation at different dosage of oxidants is depicted in Fig. 1. The control experiments were conducted under dark conditions at different pHs (4, 6, 8 or 10), where negligible Cu removal was observed (less than 2.0%). As seen in Fig. 1, both processes exhibit a self-catalyzed pattern [11], i.e., three stages can be separated from the whole degradation process, the initial induction stage, the rapid degradation stage, and the decelerated degradation stage. Meanwhile, the lower concentration of oxidants, the longer induction stage lasts. Comparatively, UV/H₂O₂ requires much longer induction time than UV/PS at different dosages. When the initial concentration of PS is 40 times higher than that of Cu(II)-EDTA, the induction stage is no longer than 5 min. When it dropped to 10 or 20, the induction stage was prolonged to ~20 min. On the contrary, the UV/H₂O₂ process requires ~90 min to initiate the rapid degradation stage even if H₂O₂ concentration is 150 times of Cu(II)-EDTA concentration. The variation of H₂O₂ and PS during the degradation is given in Fig. S1. As observed, the consumption of PS

is obviously faster than H₂O₂, which is consistent with the trend of Cu(II) removal.

TOC elimination in both processes is also depicted in Fig. 1. Similarly, the TOC removal also exhibits a typical three-stage pattern. It can be observed that at the early stage of the oxidation, the efficiency of TOC removal is always higher than that of the decomplexation in both processes. However, as the reaction proceeded, the decomplexation efficiency was increased rapidly and turned higher than TOC removal. It is possibly because the degradation intermediates formed initially (such as ED2A) are still capable of forming complexes with Cu(II) and inhibit its subsequent removal in the alkaline precipitation. With EDTA gradual degradation to low-molecular-weight compounds (such as formate and acetate), Cu(II) could be efficiently removed by alkaline precipitation. Hence, it is insufficient to evaluate the efficiency of both oxidation process in terms of Cu(II)-EDTA removal, and the final Cu(II) removal may be more appropriate to evaluate the efficiency of both oxidation processes.

3.2. Effect of pH

The effect of pH on the decomplexation of Cu(II)-EDTA in both processes is given in Fig. 2. For the UV/PS process, increasing pH from 2 to 6 does not result in an obvious difference on the final Cu removal. Further elevating pH to 8 leads to a slight deceleration of Cu reduction, and significant inhibition was observed when pH rose up to 10. Contrarily, for UV/H₂O₂, increasing pH would result in a drastic decline in Cu(II) removal, and the final Cu removal was greatly inhibited at pH = 8. As well known, SO₄²⁻ could be converted to •OH by reacting with H₂O or OH⁻. Though the transformation

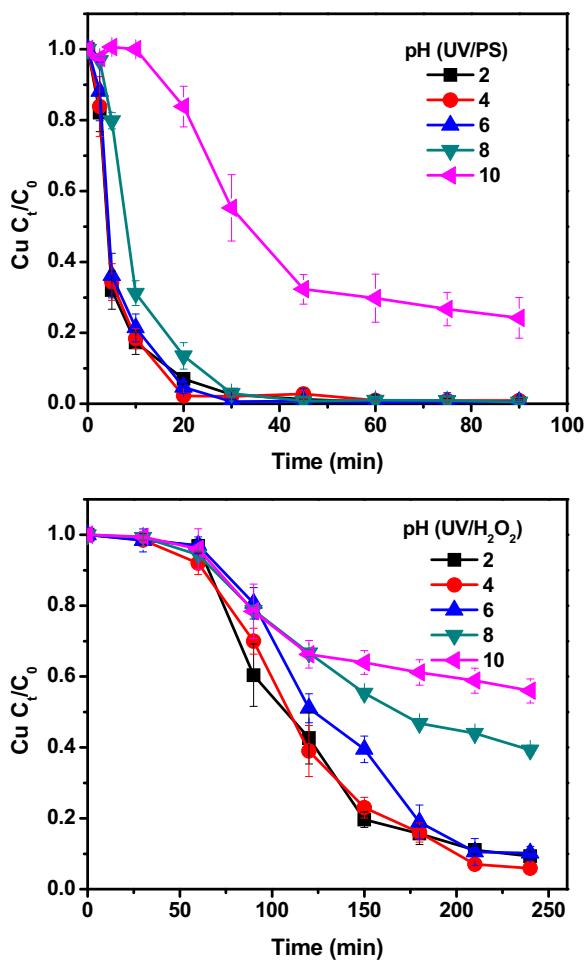


Fig. 2. Effect of pH on Cu removal in UV/PS and UV/H₂O₂ processes ([Cu(II)-EDTA]₀ = 0.3 mM, [PS]₀/[Cu(II)-EDTA]₀ = 60, [H₂O₂]₀/[Cu(II)-EDTA]₀ = 150, irradiation intensity = 0.25 mW/cm², temperature = 20 ± 1 °C).

by H₂O is usually insignificant due to its relatively low kinetics, the reaction between SO₄^{•-} and OH⁻ is crucial under basic conditions (Eqs. (3) and (4)) [30]. Fang et al. (2012) found that SO₄^{•-} was gradually converted to •OH at pH > 9, and the almost complete conversion was attained at pH = 11. Furthermore, the redox potential of •OH decreases with the elevation of pH [31]. Thus, the retardation of UV/PS at pH 8 and 10 may be partly attributed to the conversion of SO₄^{•-} to •OH. Meanwhile, altering pH would affect the reaction kinetics as well as the substrate species. The complexes may react with SO₄^{•-} faster than •OH under basic conditions, and the activation of H₂O₂ by aqueous Cu may be more efficient at acid pHs. It was reported that at alkaline pHs, Cu(III), which exhibits lower activity than •OH [32,33], was one of the major reactive species for the Cu/H₂O₂ (Cu•OH) process. In addition, Cu(III) could be converted to •OH under acid conditions (Eqs. (5)–(9)) [32]. More detailed investigation of the radicals conversion is given in Supplementary information (Text. S1 and Fig. S2).

Furthermore, (bi)carbonate was gradually accumulated in solution as the mineralization of organic ligands occurred. Theoretically, complete degradation of 0.3 mM EDTA could generate 3.6 mM (bi)carbonate. Thus, the concentration of (bi)carbonate could be several times higher than that of target ligands at the end of the reaction. Both carbonate and bicarbonate could react with SO₄^{•-} and •OH (Eqs. (10)–(13)) [34,35]. According to the rate constants, only the carbonate-mediated scavenging of •OH could substantially affect the degradation ($4 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$). Based on the pH-dependent speciation (Fig. S3), carbonate accounts for 36% of

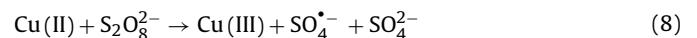
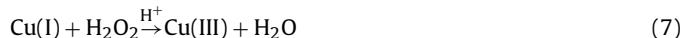
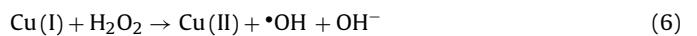
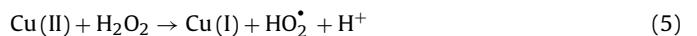
total inorganic carbon at pH 10, and the accumulation of carbonate would result in an observable inhibition of the degradation. The role of CO₃²⁻, HCO₃⁻ and reactive nitrogen species is not considered due to their relatively low formation and reactivity.



$$k[\text{H}_2\text{O}] < 2 \times 10^{-3} \text{ s}^{-1}$$



$$k = (6.5 \pm 1.0) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$



$$k = 1.6 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$



$$k = 6.1 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$



$$k = 8.5 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$$



$$k = 4 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$$

In spite of the fact that a great portion of SO₄^{•-} is converted to •OH at pH 10, the performance of UV/PS is still better than UV/H₂O₂. It is possibly because: (1). The absorption coefficient of PS and H₂O₂ at 254 nm is 20–22 and 18.6 M⁻¹ cm⁻¹, and the quantum yield of SO₄^{•-} and •OH is about 1.4–1.8 and 1.0 mol E⁻¹ respectively [36–39]. Thus, when the oxidant concentration and irradiation intensity is same, the yield of the radicals in UV/PS is approximate 0.5–1 times higher than that of UV/H₂O₂. (2) Activation of PS by Cu(II) will result in the formation of considerable concentration of Cu(III), which may also contribute to the organics degradation (Eqs. (8) and (9)), (3) The redox potential of PS (2.01 V) is higher than H₂O₂ (1.78 V) [40], implying PS has greater potential than H₂O₂ to directly oxidize Cu(II)-EDTA and its degradation products. Detailed discussion on this issue is available in Section 3.4.2, (4) the reaction pathways of both processes as well as the degradation products may be different, as discussed in the subsequent section.

In addition, we also conducted the degradation of Cu(II)-EDTA in both processes at initial pH 4 without pH adjustment during the reaction. The pH and Cu(II) variation is recorded in Fig. S4. As observed, pH increases gradually to 7.0 for UV/H₂O₂, whereas pH drops rapidly to 2.5 for UV/PS. This is reasonably because the hydroxyl ions is continuously consumed in UV/PS whereas generated in UV/H₂O₂. Similar observations were also made elsewhere [11,12,41]. It seems that pH adjustment during the reaction has negligible effect on the decomplexation efficiency in UV/PS, while Cu removal slows down with the elevation of pH in UV/H₂O₂.

3.3. Effect of coexisting substances

The effect of several commonly coexisting species, including chloride, nitrate, sulfate and natural organic matters (NOMs), was

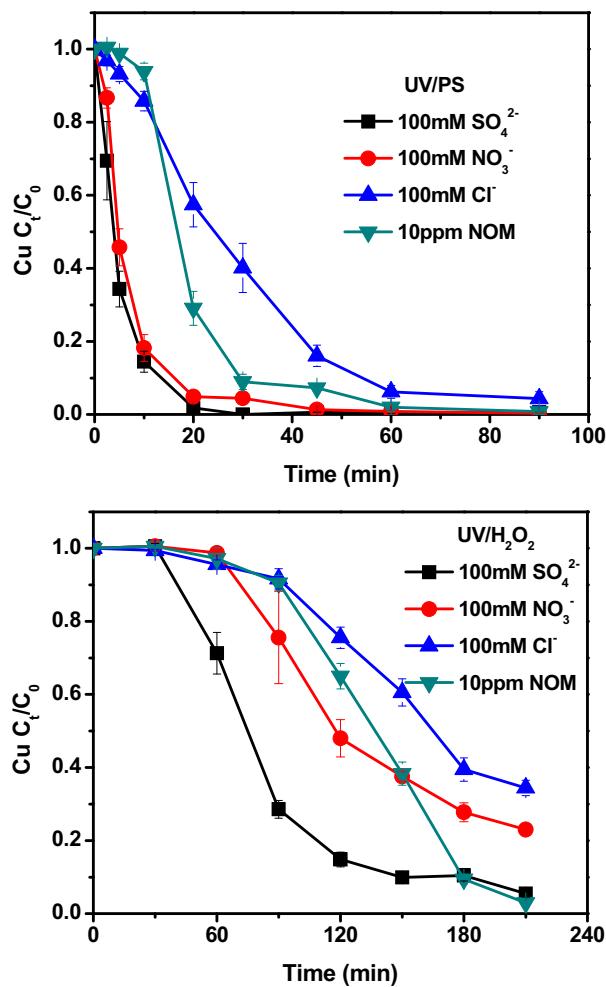


Fig. 3. Effect of common coexisting substances on Cu removal in UV/PS and UV/H₂O₂ processes ($[Cu(II)\text{-EDTA}]_0 = 0.3 \text{ mM}$, $[\text{PS}]_0/[Cu(II)\text{-EDTA}]_0 = 60$, $[\text{H}_2\text{O}_2]_0/[Cu(II)\text{-EDTA}]_0 = 150$, $\text{pH} = 4.0 \pm 0.2$, irradiation intensity = 0.25 mW/cm^2 , temperature = $20 \pm 1^\circ\text{C}$).

investigated on both oxidation processes, and the results are shown in Fig. 3. As expected, addition of sulfate has negligible influence in both processes [42], despite that SO_4^{2-} may be more sensitive to ion strength than $\cdot\text{OH}$. On the contrary, the presence of chlorine, nitrate

and NOMs inhibit the degradation efficiency and kinetics to different extents. As shown in Fig. S5, nitrate and NOM would absorb UV light at 254 nm, while the absorption is not sufficient to cause a significant influence on the photolysis of PS and H_2O_2 . Though reactive oxygen species (ROS) such as $\cdot\text{OH}$, superoxide anion ($\text{O}_2^{\cdot-}$) and triplet state oxygen ($\text{O}(3\text{p})$) could be generated during the photolysis of nitrate, the co-generated nitrite could act as radical quencher [43–45]. As a result, the presence of nitrate showed negative effect on the removal of Cu. Chloride could either impede or boost the organic degradation [46–48] through inducing the transformation of SO_4^{2-} to other oxidants such as free chlorine and $\cdot\text{OH}$. When the target substances could be readily attacked by free chlorine or $\cdot\text{OH}$, the degradation may be accelerated in the presence of chloride. In the present study, the obvious deceleration of Cu removal in the presence of chloride indicates that Cu(II)-EDTA is more favorably degraded by SO_4^{2-} and $\cdot\text{OH}$ than by free chlorine species. As for NOM, though it is capable of reducing Cu(II) [49], and the presence of quinone moieties of NOM favors the decomposition of oxidants to yield powerful radicals [50,51], it still showed adverse influence because of its capacity to scavenge radicals and stabilize heavy metals. In general, NOM reacts more quickly with $\cdot\text{OH}$ ($k = 3 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$) than SO_4^{2-} ($k = 2.35 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$) [24,52], supporting its milder influence in UV/PS process.

3.4. Mechanism of Cu(II)-EDTA degradation and Cu(II) removal

3.4.1. Degradation products of Cu(II)-EDTA

To probe the underlying mechanism for both processes to degrade Cu(II)-EDTA, the intermediates or products of Cu(II)-EDTA were detected. According to the references [7,11,53–55], two main pathways are summarized for the degradation of EDTA or metal-EDTA complexes (Fig. 4). As seen in Fig. 5a and b, Cu-ED3A and Cu-ED2A are detected, while the formation of Cu-IMDA, Cu-NTA, and Cu-glycine is negligible, demonstrating that successive decarboxylation is the dominate pathway of Cu(II)-EDTA degradation in both processes. Considering $\cdot\text{OH}$ and Cu(III) may participate in the degradation in UV/PS, we further identified the products of Cu(II)-EDTA in UV/PS with appropriate addition of TBA, an effective quencher for $\cdot\text{OH}$ ($k = 3.8 - 7.6 \times 10^8 \text{ M}^{-1} \text{s}^{-1}$) and Cu(III) ($k = 0.6 - 1.4 \times 10^7 \text{ M}^{-1} \text{s}^{-1}$) but ineffective for SO_4^{2-} ($k = 4 - 9.1 \times 10^5 \text{ M}^{-1} \text{s}^{-1}$). As shown in Fig. 5c, similar products are formed in the presence of TBA, indicating that SO_4^{2-} -mediated Cu(II)-EDTA degradation also follows the decarboxylation pathway.

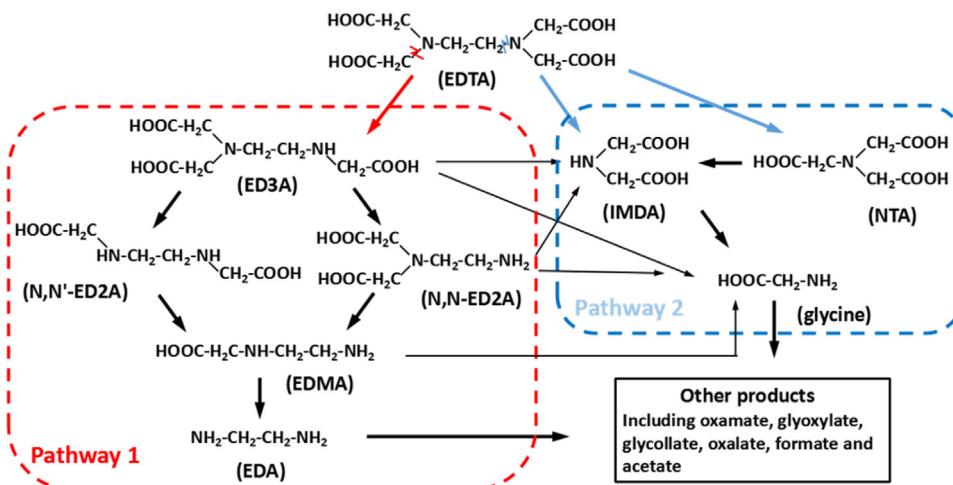


Fig. 4. Possible degradation pathway of EDTA summarized based on the available References.

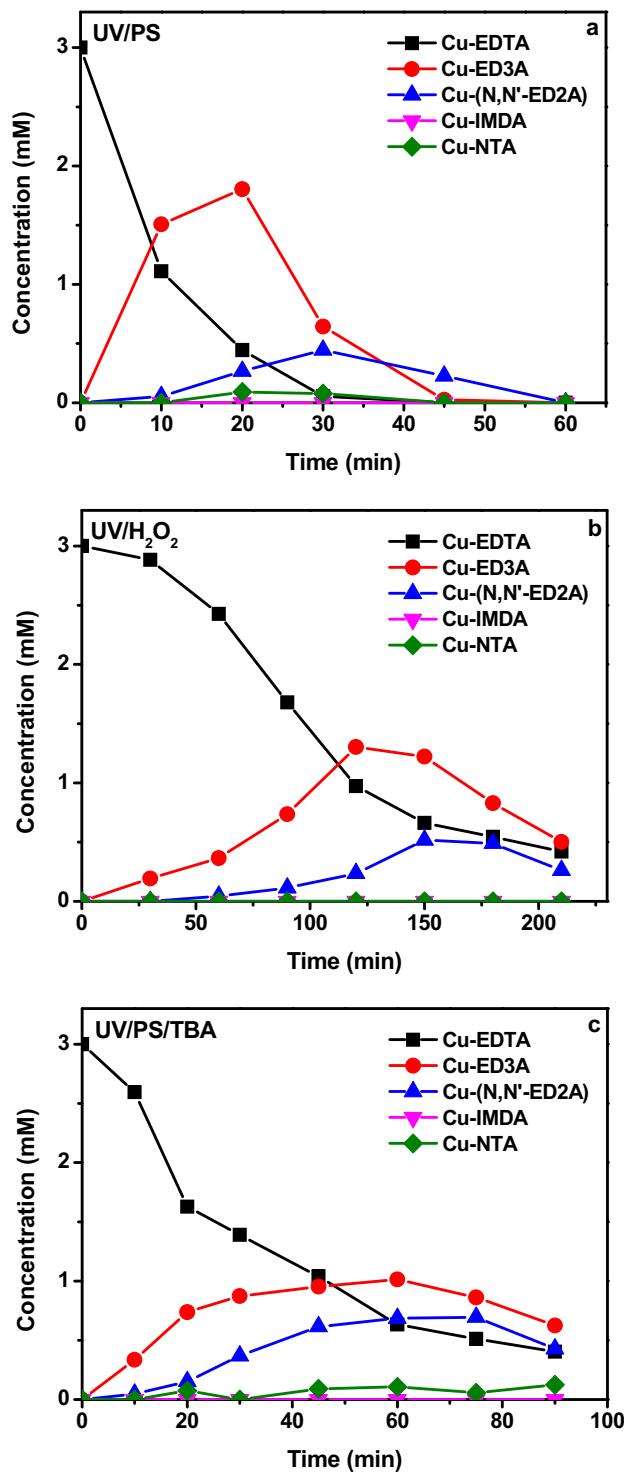


Fig. 5. Degradation products of Cu(II)-EDTA in different processes ($[Cu(II)\text{-EDTA}]_0 = 3 \text{ mM}$, $[\text{PS}]_0/[Cu]_0 = 50$, $[\text{H}_2\text{O}_2]_0/[Cu]_0 = 150$, $\text{pH} = 4 \pm 0.2$).

3.4.2. Catalyst and reaction activity of intermediates and products

Fig. 6 exhibits the EPR signal of the mixture of Cu(II)-EDTA and $\text{H}_2\text{O}_2/\text{PS}$ after irradiation for different intervals, and the control experiments were performed in the absence of Cu(II)-EDTA. Obviously, the presence of Cu(II)-EDTA significantly enhances the formation of the radicals in both processes. It indicates that during Cu(II)-EDTA degradation, the intermediates/products not only act as secondary pollutants, but also as activators of PS and H_2O_2 .

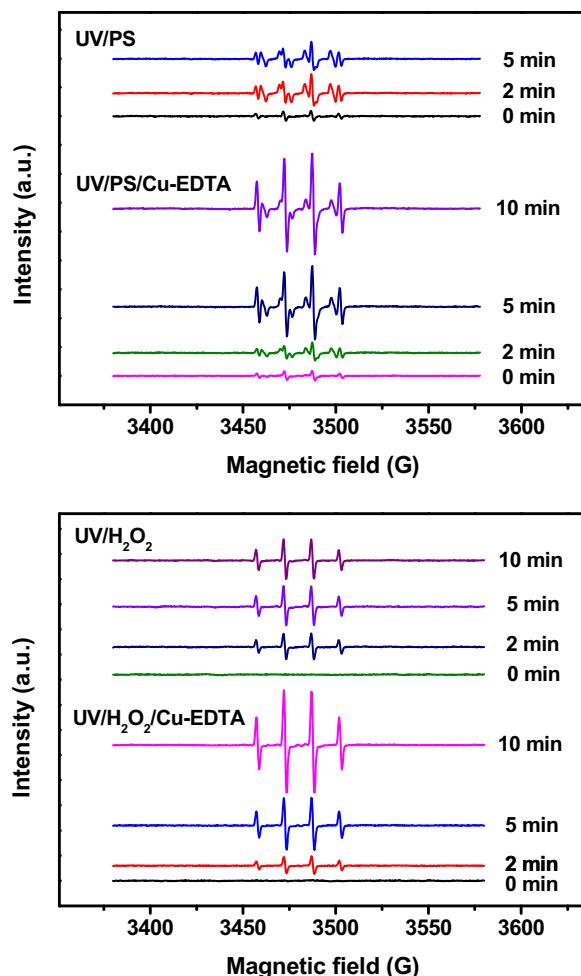


Fig. 6. EPR spectrum of mixture of Cu(II)-EDTA and PS/ H_2O_2 (and sole PS/ H_2O_2) suffered different irradiation time ($[Cu(\text{II})\text{-EDTA}]_0 = 0.3 \text{ mM}$, $[\text{PS or H}_2\text{O}_2]_0/[Cu(\text{II})\text{-EDTA}]_0 = 60$, $[\text{DMPO}]_0 = 83.3 \text{ mM}$).

This is verified by the EPR spectrum of the mixture of every possible degradation intermediate/product and $\text{H}_2\text{O}_2/\text{PS}$, as depicted in Fig. 7. It is clear that, except for Cu(II)-EDTA and Cu-NTA, most intermediates/products show great (potential) capability for PS and H_2O_2 activation. This result could well explain the accelerated degradation process. During the induction period, most Cu was present as Cu(II)-EDTA, which could not activate PS/ H_2O_2 efficiently, and the active species could be generated through the photolysis of PS/ H_2O_2 . With the reaction proceeding, Cu-EDTA was gradually degraded to its daughter compounds, such as Cu-ED2A and Cu-EDMA, which could effectively decompose PS/ H_2O_2 to yield active species. Therefore, except for photolysis, the activation of PS/ H_2O_2 by Cu-complexes made great contribution to the degradation, resulting in a rapid degradation period.

As seen in Fig. S6, only $\cdot\text{OH}$ signal was observed in UV/ H_2O_2 . In contrast, considerable intensity of $\text{SO}_4^{\cdot-}$ was also observed in UV/PS besides the $\cdot\text{OH}$ signal of similar intensity. When DMPO is used for EPR detection, the signal intensity of $\cdot\text{OH}$ is generally much stronger than $\text{SO}_4^{\cdot-}$ at the same concentration. Thus, the total reactive radicals concentration in UV/PS is much higher than UV/ H_2O_2 .

It is widely accepted that Cu(III) could be generated through the oxidation of Cu(II) by PS [56,57]. The possible formation of Cu(III) in this study was discussed in the Supplemental Information (Text S2 and Fig. S15–16). Generally, Cu(III) species is unstable and could degrade a series of compounds, including substances with carboxyl

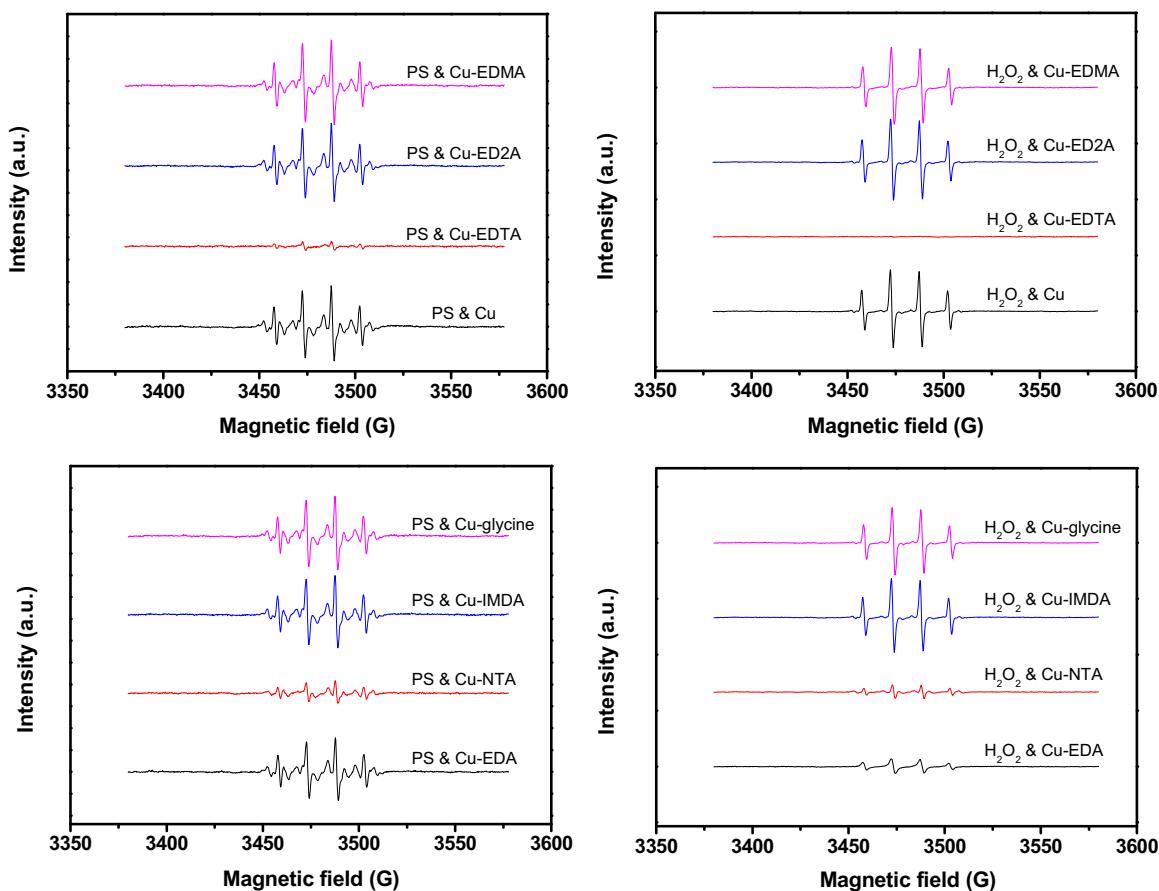


Fig. 7. EPR spectrum of mixture of PS/H₂O₂ and Cu-complex ([Cu-complex]₀ = 0.3 mM, [PS or H₂O₂]₀/[Cu-complex]₀ = 60, [DMPO]₀ = 83.3 mM).

or (and) amino group [58–60]. Thus, Cu(III) is expected to favor the degradation of Cu-complexes. On the other hand, the activity of Cu(III) is still lower than •OH and SO₄^{•-}, and its activity significantly depends on the solution chemistry [32,61–64]. Generally, Cu(III) is more active at acid conditions than neutral and alkaline circumstance [32]. Cu(III) is decomposed to Cu(II) and H₂O₂ at neutral pH and to Cu(II) and •OH under acid conditions [32,65]. Pham et al. [33] investigated the Cu(II)/H₂O₂ process and suggested that Cu(I) could be an important sink of Cu(III) due to the high kinetics of the comproportionation reaction ($k = 3.5 \times 10^9$). According to Eqs. (5)–(9), more Cu(I) and less Cu(III) will be formed in UV/H₂O₂ process, thus, it is reasonable to expect higher yield of oxidants and better degradation of organics by Cu(III) in UV/PS. Moreover, Cu(III) was suggested to be a major active species in Cu(II)/H₂O₂ system at alkaline conditions [33,66]. This may inhibit the degradation of Cu/•OH system due to its low activity at high pH.

To identify the contribution of •OH (and possible Cu(III)) on Cu removal, 30 mM TBA was added in the solution to quench •OH and Cu(III). The moderate inhibition of the final Cu removal further verified the contribution of •OH or Cu(III) for Cu-EDTA degradation in the UV/PS process (Fig. S7).

Besides •OH, SO₄^{•-} and Cu(III), Cu(II)-EDTA and its degradation intermediates/products may be directly degraded by UV irradiation or PS/H₂O₂. As shown in Fig. S8, the photolysis efficiency of each complex is below 20% in 60 min, suggesting that direct photolysis makes limited contribution to the degradation of both processes. It is also supported by the slight change of UV-vis spectrum during the UV irradiation (Fig. S9). In addition, the reaction activity between each complex and PS/H₂O₂ was identified. As depicted in Fig. S10, no noticeable degradation was observed for H₂O₂ in the presence of methanol and TBA. The presence of PS could reduce

each complex with the efficiency of <20%, indicating that the PS-mediated degradation of each Cu-complex is insignificant.

Based on the above discussion, degradation of Cu(II)-EDTA and as well as its intermediates/products are mainly through radical reactions (and possible Cu(III)), and the better performance of UV/PS than UV/H₂O₂ is mainly caused by the higher yield of reactive oxidant. Fig. S1 further manifests this point in terms of the faster consumption of PS activated by the Cu complexes. On the other side, both oxidants act not only as the source of SO₄^{•-} and •OH, but also the quenchers of radicals. For instance, •OH reacts more quickly with PS and H₂O₂ than SO₄^{•-} [24], which also accounts for the higher efficiency of UV/PS process.

3.4.3. Cu(II) removal after alkaline precipitation

Generally, alkaline precipitation is capable of removing free Cu ion as well as some Cu-complexes with weaker coordination bond energy. Fig. S11 shows the Cu removal of each Cu-complex by alkaline precipitation only. Except for several ligands of low molecule weight (such as formate, acetate, oxalate, glycollate and glyoxylate), the removal efficiency for the Cu complexes is far from satisfaction. Obviously, almost complete removal of Cu(II)-EDTA for UV/PS and UV/H₂O₂ combined with alkaline precipitation indicating that EDTA has been degraded into low-molecular-weight compounds or even mineralized.

We also obtained the structural information of the precipitate based on the XPS and XRD technique. As shown in Fig. S12, the sediment formed in both processes exhibits similar spectrum, and the presence of three peaks for elemental Cu (933.5, 942.2 and 953.5 for UV/H₂O₂, and 932.9, 941.0 and 953.5 for UV/PS) implies that Cu in both precipitates is mainly present as +2 valence and bound to oxygen. Meanwhile, Similar XRD spectrum of both precipitates (Fig.

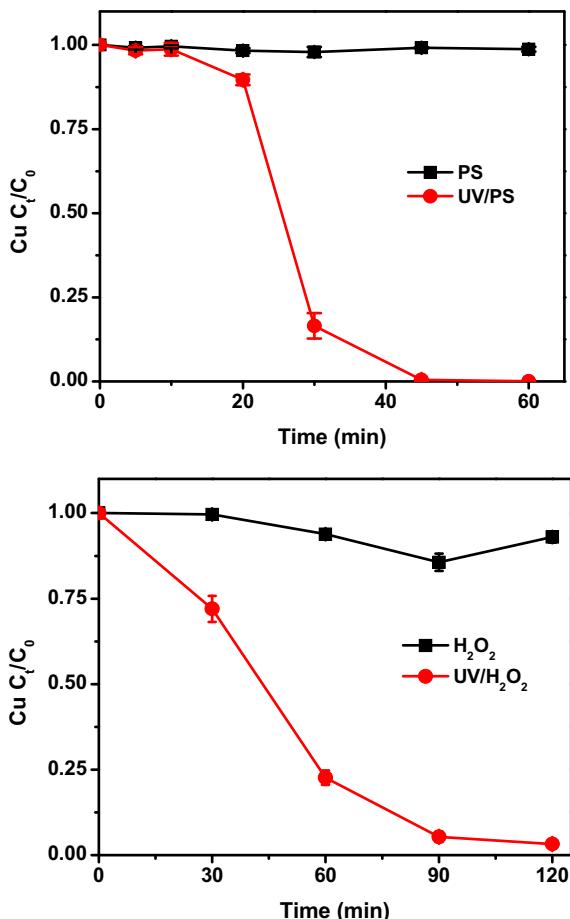


Fig. 8. Treatment of electroplating wastewater by UV/H₂O₂ and UV/PS processes ($[Cu]_0 = 0.51 \text{ mM}$, $[PS \text{ or } H_2O_2]_0/[Cu]_0 = 60$, pH during the irradiation = 3.1 ± 0.2 , precipitation pH = 11.0, irradiation intensity = 0.25 mW/cm^2 , temperature = $20 \pm 1^\circ\text{C}$).

S13) correspond well with CuO, which is consistent with the XPS spectra.

3.5. Treatment of other Cu-complexes and industrial wastewater

Except for Cu(II)-EDTA, two other Cu complexes, i.e. Cu-NTA and Cu-citrate, were chosen to further verify the performance of the combined UV/H₂O₂- or UV/PS- alkaline precipitation processes (Fig. S14). Similar Cu(II) removal of Cu-citrate to Cu-EDTA was observed, i.e., Cu could be completely removed in 45-min irradiation. As for Cu-NTA, only 5 min irradiation is required for satisfactory Cu removal. In addition, a real wastewater sampled from an electroplating plant in Huizhou, Guangdong Province (China), was also employed for treatment by the above combined processes (initial $[Cu]_0 = 0.51 \text{ mM}$, TOC = 109 mg/L and pH = 3.1). As shown in Fig. 8, negligible Cu removal was found when PS or H₂O₂ was added in the absence irradiation, implying that Cu in the wastewater is well “protected” by the organic ligands. For the UV/PS combined process, the residual Cu was below the detection limit (<0.03 mg/L) in the effluent after 45 min irradiation. By contrast, Cu(II) is still present in wastewater after treatment by UV/H₂O₂ process even after 120-min irradiation. Such different performance of both combined processes further demonstrated that UV/PS-alkaline precipitation is a promising strategy for removal of Cu complex from wastewater.

4. Conclusions

In this study, a SO_4^{2-} based AOP, i.e., UV/PS process, followed by an alkaline precipitation, was proposed to dispose of Cu(II)-EDTA from water. The UV/H₂O₂ process was employed for comparison purpose. Some conclusions could be drawn from this study:

- 1.) Cu(II)-EDTA degradation by UV/PS is much faster than UV/H₂O₂ under the same oxidant dosage, and the induction time for UV/PS is greatly shorter.
- 2.) The optimal pH for UV/PS and UV/H₂O₂ processes is 2–8 and 2–6 respectively. The coexisting substances (Cl[−], NO₃[−] and NOMs) exhibited less inhibition on the Cu-EDTA degradation UV/PS than by UV/H₂O₂.
- 3.) Both SO_4^{2-} and $\cdot\text{OH}$ induce the degradation of Cu(II)-EDTA via successive decarboxylation pathway. $\cdot\text{OH}$ was detected in both processes, while considerable yield of SO_4^{2-} was observed in UV/PS only. Radicals yield of UV/PS is much higher than UV/H₂O₂.
- 4.) Direct photolysis and reaction with PS/H₂O₂ make limited contribution to the degradation. Cu(II) could be well precipitated when EDTA is degraded to low-molecular-weight ligands or mineralized.
- 5.) UV/PS process is capable of degrading Cu-NTA and Cu-citrate and exhibits higher efficiency than UV/H₂O₂. The proposed UV/PS-alkaline precipitation process is efficient in removing Cu(II)-organic complexes from the electroplating effluent.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.07.023>.

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